Developing Nanoscience Tools for Li-ion Battery Research

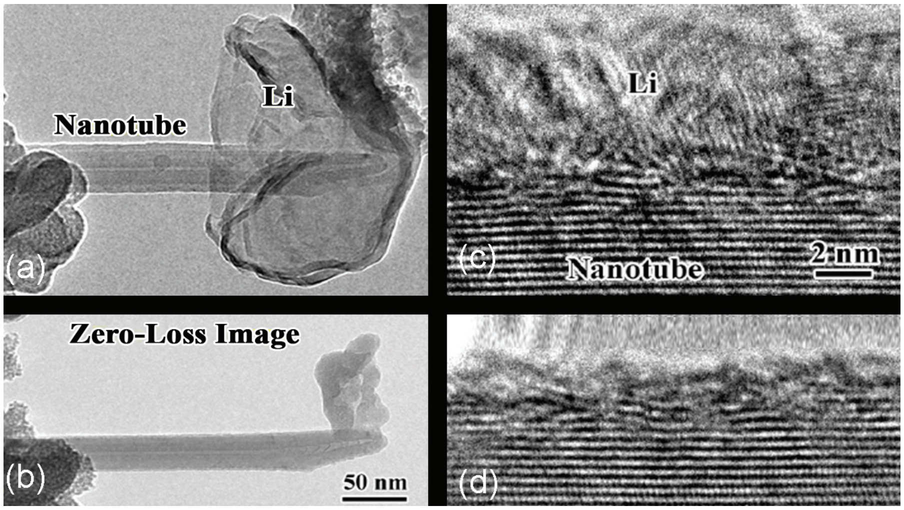

Figure 1: HRTEM images of the solid-state reaction between Li metal and a multi-wall carbon nanotube (MWCNT). (a) A Li particle in contact with the MWCNT reacts by diffusion and insertion between the walls of the MWCNT in approximately one minute (b). This process is imaged with atomic resolution near the start of contact (c) and after reaction completion, (d). An expansion of the inter-wall spacing is observed in (d).

Significant improvements in battery performance will require detailed, nanoscale studies of electrochemical materials

For more information:

Technical Contact:
John Sullivan
505-845-9496
jpsulli@sandia.gov

Science Matters Contact:
Alan Burns
505-844-9642
aburns@sandia.gov

In order to meet our nation's goals for energy efficiency and green energy production, major improvements are needed in electrical energy storage. The rechargeable Li-ion battery is widely recognized as offering the best energy-to-weight performance (an important metric in portable applications). The success of Li-ion batteries is due to years of careful development of the anodes, cathodes, and separator materials. However, in order to meet broad application goals requiring a factor of two increase in performance, these material systems and architectures will need to change significantly.

The research challenge is that the materials that are currently used, as well as those that are proposed, are often a mixture of multiple phases of nanoscale to microscale dimension, and it is exceedingly difficult to directly measure the structure and electrochemical performance at these length scales. Thus Sandia is developing tools and capabilities to measure the structural changes and electrochemical behavior of Li-ion battery materials during active charge-discharge cycling down to the single-particle level and with atomic to nanoscale spatial resolution. To achieve this, researchers have developed microfabricated platforms to isolate individual nanoparticle battery components and permit their characterization during electrochemical cycling inside a high-resolution transmission electron microscope (HRTEM).

Sandia has developed two approaches to perform electrochemistry inside the high vacuum of the HRTEM: (1) "open cells" using ionic liquid electrolytes, and (2) "sealed cells" that are created using microelectromechanical systems (MEMS) processed at the MESA (Microsystems and Engineering Sciences Applications) Facility. As a first step towards "open cell" electrochemistry inside a HRTEM, researchers have examined the sequence of lithium insertion in multi-wall carbon nanotubes (MWCNT) via solid-state reaction (sans electrolyte), as shown in Figure 1a-d. A particle of lithium metal was placed in

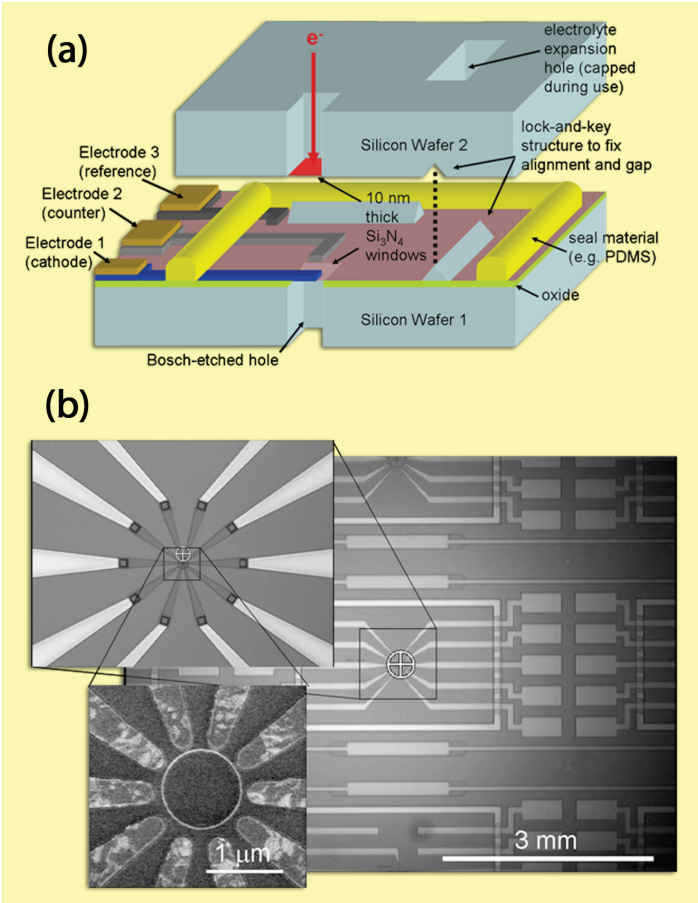

Figure 2: (a) A schematic of the sealed electrochemistry cell for HRTEM studies of battery electrochemical processes. The platform is constructed using a flip-chip approach combing two MEMS chips that encapsulate a thin layer of electrolyte between electron-transparent windows. (b) Images of the lower chip of the platform showing the dense array of closely-spaced electrodes. This electrode geometry enables DEP of nanoscale battery materials.

contact with a MWCNT using a nanomanipulator inside the HRTEM (Figure 1a). In approximately one minute of imaging, the lithium reacts with carbon and intercalates between the walls of the MWCNT (Figure 1b). This process is followed with atomic resolution (Figures 1c and 1d), where an increase in the interwall spacing of the nanotube is observed, consistent with lithium intercalation. This experiment is currently being repeated with an ionic liquid electrolyte separating the lithium metal and MWCNT, permitting liquid electrochemical studies inside the HRTEM.

Researchers are also interested in imaging the formation process and spatial distribution of the solid-electrolyte-interphase, a reaction product between the battery electrodes and ethylene carbonate-based electrolytes. In order to use the electrolyte inside the vacuum environment of TEM, Sandia applied MEMS technology to develop sealed electrochemical cells (Figure 2). The sealed platform is created by bonding two chips using a flip-chip approach, with the bottom chip containing a dense array of buried electrical interconnects that permit electrical contact to battery materials. Figure 2(b) shows the bottom chip and a close-up of the electrical interconnect structure designed to permit the assembly, via dielectrophoresis (DEP), of nanoparticles and nanowires across a narrow electron-transparent aperture. In DEP, AC electric fields enable the placement of individual nanoparticles and nanowires, initially suspended in solution, across the narrow electrode gaps. Figure 3(a) shows electron microscopy images of DEP-assembled nanostructures across gaps. This technique thus isolates individual nanoscale battery materials and enables studies of their electrochemical performance.

This work is creating new tools for understanding the electrochemical processes of nanoscale battery materials during real-time operation. This is an important capability that will aid in understanding the degradation processes in existing Li-ion batteries, as well as aiding in the development of new, higher performance battery materials. Examples of these new materials include conversion anode materials, based on silicon, tin oxide, and iron oxide, and new high voltage cathode materials, such as $LiNiPO_4$. Without this new characterization capability, much of the battery development will occur without understanding the mechanisms, and this could lead to unexpected pitfalls or missed opportunities for improvement. Ultimately, the development of a high performance energy storage technology will enable practical electric vehicles, miniaturized remote sensors, and more practical green energy technologies by leveling the short-frequency variations in power production.

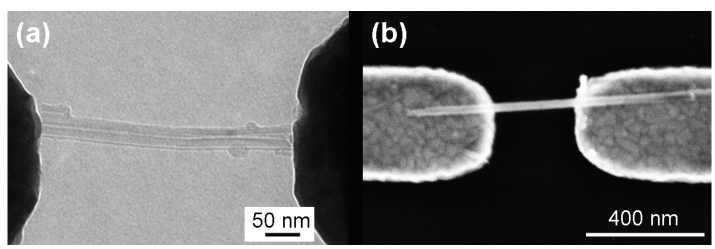

Figure 3: Examples of using DEP to assemble battery electrode materials. (a) HRTEM images of a multi-wall carbon nanotube placed across a silicon nitride electron-transparent membrane. (b) A SEM image of a MnO_2 nanowire spanning an electrode gap. When reacted with Li, MnO_2 is a common Li-ion cathode material.

Sandia National Laboratories

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